

## KMnAg<sub>3</sub>(CN)<sub>6</sub>, a new triply interpenetrating network solid

Urs Geiser\* and John A. Schlueter

Materials Science Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Correspondence e-mail: ugeiser@anl.gov

Received 17 December 2002

Accepted 14 January 2003

Online 18 February 2003

The single-crystal structure of potassium manganese tris[dicyanoargentate(I)], KMnAg<sub>3</sub>(CN)<sub>6</sub>, is described. This is the first Mn-containing example of the triply interpenetrating MAg<sub>3</sub>(CN)<sub>6</sub> type. The K<sup>+</sup> ion is found to be located in an ordered manner on one of two possible interstitial sites, leading to a chiral space group.

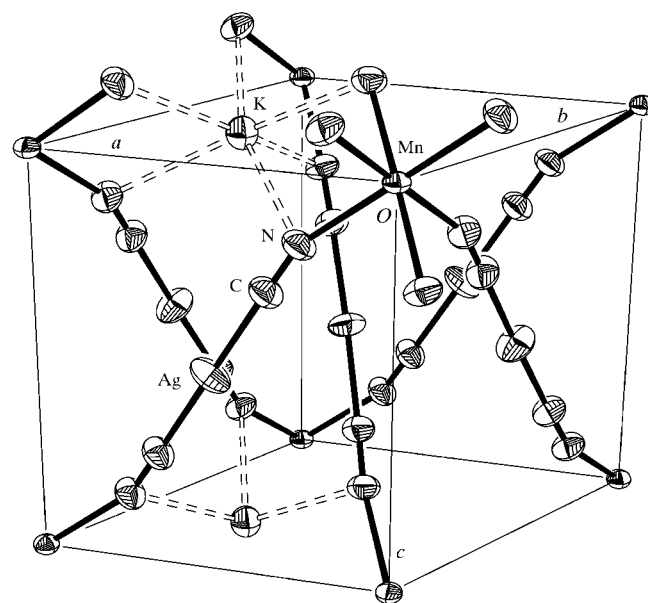
### Comment

The construction of three-dimensional and interpenetrating lattices is a contemporary challenge for crystal engineering (for a review of interpenetrating networks, see Batten & Robson, 1998). Transition metals can be conveniently linked through the use of pseudohalides, leading to the formation of such polymeric networks. The magnitude of magnetic superexchange in pseudohalide-based coordination polymers has remained an area of active research interest. While the cyanide and dicyanamide anions have been extensively studied in this regard, much less is known about related structures incorporating the dicyanoargentate anion, the high aspect ratio of which makes it ideal for the formation of interpenetrating structures. We are interested in the crystallization of magnetic anionic networks and chose to study the dicyanoargentate anion, a nearly linear analog to the bent dicyanamide ligand, as a building block for cyano-bridged heterobimetallic complexes.

Pauling & Pauling (1968) suggested that very large open cubic frameworks of the type  $M[\text{Ag}(\text{CN})_2]_3$  can be prepared through the incorporation of large neutral molecules in the center of the cubes. Alternatively, doubly or triply interpenetrating lattices can be formed to fill the voids. While attempting to crystallize the three-dimensional anionic network  $\text{Mn}[\text{Ag}(\text{CN})_2]_3^-$ , in which a tetrapropylammonium cation would fill the cubic void, the title salt  $\text{KMnAg}_3(\text{CN})_6$  formed instead.

The structure of  $\text{KMnAg}_3(\text{CN})_6$  consists of three interpenetrating trigonally distorted cubic lattices of composition  $\text{MnAg}_3(\text{CN})_6^-$  and intercalated  $\text{K}^+$  ions. The six-coordinate Mn atoms occupy the corners of the cubes, whereas the two-

coordinate Ag atoms are found in the middle of the cube edges. The cyanide groups bridge between the Mn and Ag atoms. Alternatively, the structure can be thought of as being composed of close-packed double layers of cyanide ions, with one third of the octahedral holes filled by Mn, and another third by K atoms. The C atoms of the cyanide groups protrude out of the double layer in a tilted direction (along the  $a+c$  diagonal), and  $\text{Ag}^+$  ions then bridge the double layers *via* C–Ag–C bonds.

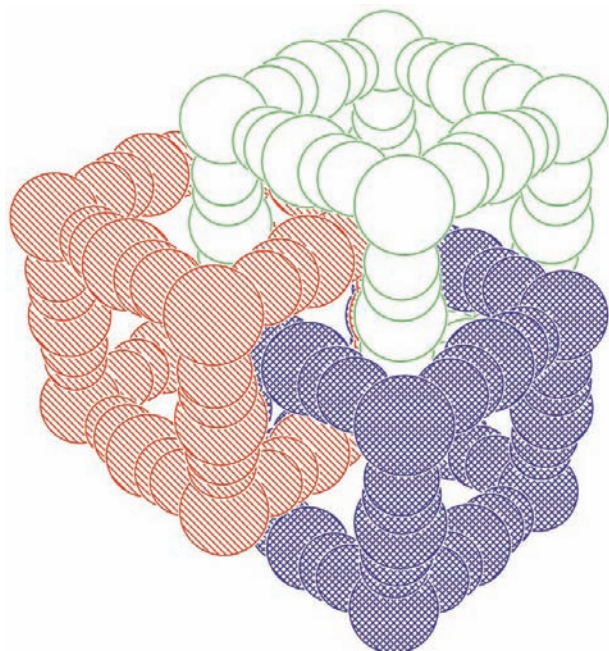


**Figure 1**

The unit-cell packing of  $\text{KMnAg}_3(\text{CN})_6$ , shown with 50% probability displacement ellipsoids. The coordination spheres of one Mn and one K atom are completed outside the unit cell for clarity, using broken bonds. The three interpenetrating networks are represented by the solid bonded strands  $(a,b,0)$  to  $(0,0,c)$ ,  $(a,b,0)$  to  $(0,0,0)$  to  $(0,b,c)$ , and  $(a,0,0)$  to  $(a,b,c)$  to  $(0,b,0)$ .

We have carefully established (see *Experimental*) that the cyanide groups bind to Mn through the N atoms and to Ag through the C atoms. This assignment is also consistent with the observed bond lengths of 2.060 (2) Å for Ag–C and 2.236 (1) Å for Mn–N. These short Ag–C and relatively long Mn–N bond lengths are consistent with other cyanide-bridged Mn–Ag systems, *e.g.* *catena*-{tetrakis( $\mu_2$ -cyano)bis-[2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide]-disilvermanganese(II)} (Dasna *et al.*, 2001), where the corresponding values are 2.060–2.072 and 2.252–2.253 Å, respectively. The site symmetry on the Mn center is 32, with a small trigonal distortion from octahedral symmetry corresponding to a rotation of the ‘top’ *versus* the ‘bottom’ (with respect to the  $ab$  plane) N3 triangle of 1.5 (1)° and a 5.0 (2)% elongation along the  $c$  axis. The distortion at the K site is much more severe, *i.e.* a rotation of 20.9 (1)° and a 19.8 (2)% trigonal flattening. Except for the K atom, the deviations from  $P\bar{3}1m$  symmetry are slight, *e.g.* the  $\text{Ag}(\text{CN})_2^-$  group is essentially linear (Table 1), and the *trans*-N–Mn–N angles are 178.8 (1)°.

A similar triply interpenetrating  $M\text{Ag}_3(\text{CN})_6$  network has been found in a number of compounds, *e.g.*  $\text{CoAg}_3(\text{CN})_6$  (Pauling & Pauling, 1968; Ludi & Güdel, 1968),  $\text{K}_2\text{NaAg}_3(\text{CN})_6$  (Zabel *et al.*, 1989), and  $\text{RbCdAg}_3(\text{CN})_6$  (Hoskins *et al.*, 1994), but the title compound is the first example containing the  $\text{Mn}^{2+}$  ion at the six-coordinate site. In the first two examples, the symmetry is  $P\bar{3}1m$ , because the two extra octahedral sites are either both empty or both filled. In contrast,  $\text{RbCdAg}_3(\text{CN})_6$  is isomorphous with the title compound, as is gold-containing  $\text{KCoAu}_3(\text{CN})_6$ , with a demonstrated piezoelectric effect as proof for the non-centrosymmetric crystal symmetry (Abrahams *et al.*, 1980). In  $\text{KAg}(\text{CN})_2$  (Hoard, 1933) and  $\text{KAu}(\text{CN})_2$  (Rosenzweig & Cromer, 1959), all octahedral holes are filled, but the sequence of double layers contains additional shifts, therefore leading to a doubling and tripling, respectively, of the *c* axis. Interestingly,  $\text{CoAg}_3(\text{CN})_6$  is the only salt in the series where the Co ion was assumed, without discussion by either group of authors (Pauling & Pauling, 1968; Ludi & Güdel, 1968), to be bonded to the C atom of the cyanide group. It would be interesting to examine whether this assumption holds in a rigorous refinement of diffraction data obtained by the use of modern instrumentation.



**Figure 2**

A space-filling packing diagram of the three interpenetrating networks of  $\text{KMnAg}_3(\text{CN})_6$  (shown in three different shading styles), viewed approximately along the trigonal axis. A more artistic rendering of this view may be found in the supplementary material.

### Experimental

Tetrapropylammonium bromide (Aldrich, 532 mg, 2 mmol) was dissolved in absolute ethanol (10 ml) and potassium dicyanoargentate(I) (Aldrich, 1194 mg, 6 mmol) was dissolved in water (15 ml). These two solutions were combined and layered on top of an aqueous solution (10 ml) of manganese(II) nitrate hydrate (Aldrich, 358 mg, 2 mmol). Colorless hexagonal plates of  $\text{KMnAg}_3(\text{CN})_6$  formed within 1 d.

### Crystal data

$\text{KMnAg}_3(\text{CN})_6$   
 $M_r = 573.77$   
 Trigonal,  $P312$   
 $a = 6.9219$  (10) Å  
 $b = 6.9219$  (10) Å  
 $c = 8.1465$  (16) Å  
 $V = 338.03$  (10) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 2.819$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 772 reflections  
 $\theta = 3.4\text{--}28.2^\circ$   
 $\mu = 5.48$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Hexagonal plate, colorless  
 0.46 × 0.32 × 0.03 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 Area-detector  $\omega$  scans  
 Absorption correction: by integration (*XPREP* in *SHELXTL*; Sheldrick, 2001)  
 $T_{\min} = 0.155$ ,  $T_{\max} = 0.829$   
 3417 measured reflections  
 558 independent reflections

551 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 28.2^\circ$   
 $h = -8 \rightarrow 9$   
 $k = -8 \rightarrow 9$   
 $l = -10 \rightarrow 10$   
 77 standard reflections  
 frequency: 900 min  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.012$   
 $wR(F^2) = 0.032$   
 $S = 1.11$   
 558 reflections  
 30 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.0080P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXTL* (Sheldrick, 2001)  
 Extinction coefficient: 0.058 (2)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.18 (4)

**Table 1**

Selected geometric parameters (Å, °).

|                                      |             |                       |             |
|--------------------------------------|-------------|-----------------------|-------------|
| Ag—C                                 | 2.0599 (16) | K—N                   | 2.9266 (18) |
| Mn—N                                 | 2.2365 (13) | C—N                   | 1.138 (2)   |
| $C^i$ —Ag—C                          | 178.05 (15) | N—K—N <sup>vii</sup>  | 66.75 (5)   |
| N <sup>ii</sup> —Mn—N                | 93.76 (9)   | N—K—N <sup>viii</sup> | 100.27 (4)  |
| N <sup>ii</sup> —Mn—N <sup>iii</sup> | 178.78 (10) | N—C—Ag                | 178.3 (2)   |
| N—Mn—N <sup>iii</sup>                | 87.08 (5)   | C—N—Mn                | 159.36 (14) |
| N <sup>iii</sup> —Mn—N <sup>iv</sup> | 92.08 (9)   | C—N—K                 | 96.52 (14)  |
| N <sup>v</sup> —K—N                  | 95.15 (7)   | Mn—N—K                | 100.58 (5)  |
| N <sup>vi</sup> —K—N                 | 161.53 (6)  |                       |             |

Symmetry codes: (i)  $1 - x + y, y, 1 - z$ ; (ii)  $-y, -x, -z$ ; (iii)  $-y, x - y, z$ ; (iv)  $-x + y, y, -z$ ; (v)  $1 - x + y, y, -z$ ; (vi)  $1 - y, 1 - x, -z$ ; (vii)  $x, x - y, -z$ ; (viii)  $1 - x + y, 1 - x, z$ .

The crystal structure was initially solved by direct methods in space group  $P\bar{3}$ . After inspection with the routine *MISSYM* (Le Page, 1987, 1988) in the program *PLATON* (Spek, 1990), we added a vertical mirror plane and concomitant twofold axis to arrive at space group  $P\bar{3}1m$ . Refinement in this space group (with half-occupied disordered K atoms) converged at  $R_1 = 0.053$  and  $wR_2 = 0.218$ , with peaks on the difference map of +2 (near Ag) and  $-3$  e Å<sup>-3</sup> (near C). Subsequently, the inversion center was removed and only one of the now inequivalent K positions was retained, leading to the final refinement in space group  $P312$ . We also explored the effect of exchanging the C and N atoms in space group  $P312$ . This led to convergence at  $R_1 = 0.028$  and  $wR_2 = 0.088$ , peaks of +1 (near C) and  $-1$  e Å<sup>-3</sup> (near N), and highly dissimilar atomic displacement parameters for the C and N atoms, so the assignment listed in the tables

here was accepted as correct. The chirality of the crystal resulted in a Flack (1983) parameter of 0.18 (4), which was interpreted and included in the refinement as racemic twinning of the same volume fraction. The 234 Friedel pairs were not merged in the final refinement.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work at Argonne National Laboratory was sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1004). An additional figure is also available. Services for accessing these data are described at the back of the journal.

## References

- Abrahams, S. C., Bernstein, J. L., Liminga, R. & Eisenmann, E. T. (1980). *J. Chem. Phys.* **73**, 4585–4590.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1461–1494.
- Bruker (2001). *SAINT*. Version 6.28a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dasna, I., Golhen, S., Ouahab, L., Daro, N. & Sutter, J.-P. (2001). *Polyhedron*, **20**, 1371–1374.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hoard, J. L. (1933). *Z. Kristallogr.* **84**, 231–255.
- Hoskins, B. F., Robson, R. & Scarlett, N. V. Y. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2025–2026.
- Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
- Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.
- Ludi, A. & Güdel, H. U. (1968). *Helv. Chim. Acta*, **51**, 1762–1765.
- Pauling, L. & Pauling, P. (1968). *Proc. Natl Acad. Sci.* **60**, 362–367.
- Rosenzweig, A. & Cromer, D. T. (1959). *Acta Cryst.* **12**, 709–712.
- Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Zabel, M., Kühnel, S. & Range, K.-J. (1989). *Acta Cryst.* **C45**, 1619–1621.